

Partial oxidation reforming of simulated biogas in gliding arc discharge system

Patipat Thanompongchart / Parin Khongkrapan / Nakorn Tippayawong

RECEIVED 17 MAY 2013; ACCEPTED AFTER REVISION 6 NOVEMBER 2013

Abstract

Plasma assisted, partial oxidation reforming of biogas is considered to be a promising technology to produce synthesis gas. In this work, a 0.1 kW gliding arc plasma reformer was employed to investigate the effects of biogas composition and oxygen availability on CH_4 and CO_2 conversions, as well as the product distribution. Air was used in the partial oxidation of biogas. The results showed that at low CH_4/O_2 ratio or high oxygen availability, increasing CH_4 content appeared to show higher H_2 yield and CH_4 conversion. Increasing CH_4/O_2 ratio adversely affected H_2 and CO yields, and CH_4 conversion. Optimum condition was found at CH_4/CO_2 of 90:10 and CH_4/O_2 of 1.2 for the maximum CH_4 conversion and H_2 yield of 45.7 and 25.3%, respectively.

Keywords

biomass • methane reforming • non-thermal plasma • renewable energy • synthesis gas

Acknowledgement

This work is financially supported by the Commission on Higher Education under National Research University project. Support from the Thailand Research Fund for PT under a Royal Golden Jubilee PhD program is acknowledged.

1 Introduction

Energy is recently becoming one of the most pressing issues in many societies and countries. It affects wellbeing of the people, economic development, national security, and civilization. The energy demand remains high and growing, while conventional supply from crude oils is increasingly fragile. Concerns over climate change and recent incidents at Fukushima have presently made coal and nuclear powers rather unfashionable. To tackle a major threat of energy crisis, strong energy conservation and efficiency improvement program must be adopted. At the same time, alternative energy sources must be explored and utilized. Renewable energy is, if properly integrated, able to cover all energy needs. Change from fossil fuels to renewables is happening and relevant to many nations around the World.

Among various types of renewable energy resources, biogas appeared to be one of the most promising options. Thailand has the potential to produce over one billion m^3 of biogas a year from its agricultural industry alone [1]. Normally, biogas contains 45-70% CH_4 , 30-45% CO_2 , and a trace amount of other gases. Composition of biogas depends on raw biomass materials and conditions of anaerobic digestion [2,3]. The biogas produced is generally utilized at farm levels for heating, mechanical shaft works, and electricity generation. To further harness this renewable energy source, biogas may be upgraded to more attractive and marketable gaseous fuels such as compressed biogas, biomethane, or synthesis gas [1,4,5].

Synthesis gas (H_2 and CO) production is of great interest because it can be used as starting feed to generate synthetic chemicals and liquid fuels [6,7]. There are several technologies available for synthesis gas production through CH_4 rich gas, namely, steam or wet reforming, CO_2 or dry reforming, and partial oxidation reforming, shown in eqs. (1) to (3) below;



Patipat Thanompongchart

Parin Khongkrapan

Nakorn Tippayawong

Department of Mechanical Engineering, Faculty of Engineering,

Chiang Mai University, Chiang Mai 50200, Thailand

e-mail: n.tippayawong@yahoo.com

Because the former two routes are highly endothermic, hence require heat input and consume large amount of energy, considerable attention has been drawn to focus on the exothermic partial oxidation. For non-catalytic partial oxidation of hydrocarbons, it usually occurs at high temperature (1300-1500°C) to complete conversion. In biogas reforming, methane decomposition and boundary reactions (4 and 5) are possible,



For biogas, combination of carbon dioxide and partial oxidation of methane can reduce coke deposition on electrodes' surface. Furthermore, application of plasma technology may enable high conversion at reduced energy consumption of the chemical process [8].

Plasma is ionized gas that can be generated from combustion, electric discharges (arc, spark, plasma jet, microwave discharge, corona, glow and radio frequency), and shocks (electrically, magnetically and chemically driven) [9]. It is effective in generating active species such as electrons, ions, and radicals. It can be classified into non-thermal and thermal plasma. Non-thermal plasma has low electron density ($< 10^{19} \text{ m}^{-3}$) and dissimilarity between electron and heavy particle temperatures. Inelastic collisions between electrodes and heavy particles create the plasma reaction species whereas elastic collisions heat the heavy particle [8,10,11]. Advantage of using non-thermal plasma is associated with lower temperatures, lower energy consumption and electrode erosion [12]. Gliding arc discharge is one of non-thermal plasma, associated with low reaction temperature, high selectivity, and compact equipment [12–14]. It has at least two diverging knife shaped electrodes. When a high voltage is applied, a relatively low current arc discharge is formed repeatedly at the narrowest gap across the electrodes, and spreads along the edges, and eventually disappears downstream.

Gliding arc plasma has been utilized in reforming of CH_4 rich gas to produce synthesis gas [10,13]. But, there have been relatively few studies investigating plasma assisted partial oxidation of CH_4/CO_2 system. Reported works using gliding arc discharge reactor were even more limited. Notable article on gliding arc plasma reforming of biogas include Sreethawong et al. [15], Yang et al. [16], Rafiq and Hustad [17,18], and Rafiq et al. [19]. It was noted that none of these works focused on non-catalytic effect at high CH_4/O_2 ratios. In this work, biogas reforming via partial oxidation under gliding arc plasma was carried out. The main objective is to explore partial oxidation of biogas to produce synthesis gas. Effects of biogas composition and rich fuel-to-air mixing on process performance were investigated.

2 Materials and Methods

Fig. 1 shows schematic diagram of the experimental setup for plasma reforming of biogas. It consists of a gliding arc reactor, a power supply, gas feeding line, measurement and analysis instrumentation. Simulated biogas was generated from mixing CH_4 and CO_2 . Air was used as source of oxygen in partial oxidation. These gases were of research grade obtained from Thai Industry Gas Plc. The feed gas line was responsible for supplying CH_4 , CO_2 and air. The main input gases were controlled by Dwyer VFA gas flow meters and regulators as well as Hewlett-Packard soap film flow meter. It was injected through a cylindrical tube with diameter of 1 mm with total flow rate of 1 L/min. The reactor was made of transparent acrylic and glass plates. Knife shaped electrodes were made from stainless steel (3 mm thick). The electrode gap was 4 mm. The input power was supplied from an AC high voltage (HV) Lecip Neon transformer was fixed at 7.5 kV and 100 W. The analysis system was divided into electrical characterization, temperature measurement, and gas analysis. The electrical measurement consists of Fluke 80K-40 HV probe, Gwinstek GOS-620 oscilloscope and Pro Elec PL09564 power meter to measure the supplied electric power. The temperature measurement was carried out using Digicon ND-400N type K thermocouples. The temperature was monitored in real time from the thermocouples installed in the electrode gap, avoiding contact with electrodes and discharge region. The gas analysis was done by a Shimadzu 8A gas chromatography equipped with a thermal conductivity detector and Shin carbon column, able to analyze H_2 , O_2 , N_2 , CO , CH_4 and CO_2 .

Feed gas composition can be adjusted. Once constant composition of mixed gas passed into the gliding arc plasma reactor was established, the power supply was then switched on. The system was allowed to stabilize, then gas samples up- and downstream of the reactor were collected in Restek multilayer foil gas bags, and sent immediately for analysis. At least three experimental runs were carried out for each case, and average results were shown. Effect of the following parameters on reforming reaction were studied; biogas composition (CH_4/CO_2 : 50/50, 70/30, 90/10) and oxygen content in partial oxidation process (CH_4/O_2 : 0.5 – 20). To evaluate the performance of the process, equations (6) to (12) were used;

$$\text{CH}_4 \text{ conversion: } C_{[\text{CH}_4]}(\%) = \frac{M_{[\text{CH}_4, \text{in}]} - M_{[\text{CH}_4, \text{out}]}}{M_{[\text{CH}_4, \text{in}]}} \times 100 \quad (6)$$

$$\text{CO}_2 \text{ conversion: } C_{[\text{CO}_2]}(\%) = \frac{M_{[\text{CO}_2, \text{in}]} - M_{[\text{CO}_2, \text{out}]}}{M_{[\text{CO}_2, \text{in}]}} \times 100 \quad (7)$$

$$\text{H}_2 \text{ selectivity: } S_{[\text{H}_2]}(\%) = \frac{M_{[\text{H}_2, \text{produced}]}}{2 \times M_{[\text{CH}_4, \text{converted}]}} \times 100 \quad (8)$$

$$\text{CO selectivity: } S_{[\text{CO}]}(\%) = \frac{M_{[\text{CO}, \text{produced}]}}{M_{[\text{CH}_4, \text{converted}]}} \times 100 \quad (9)$$

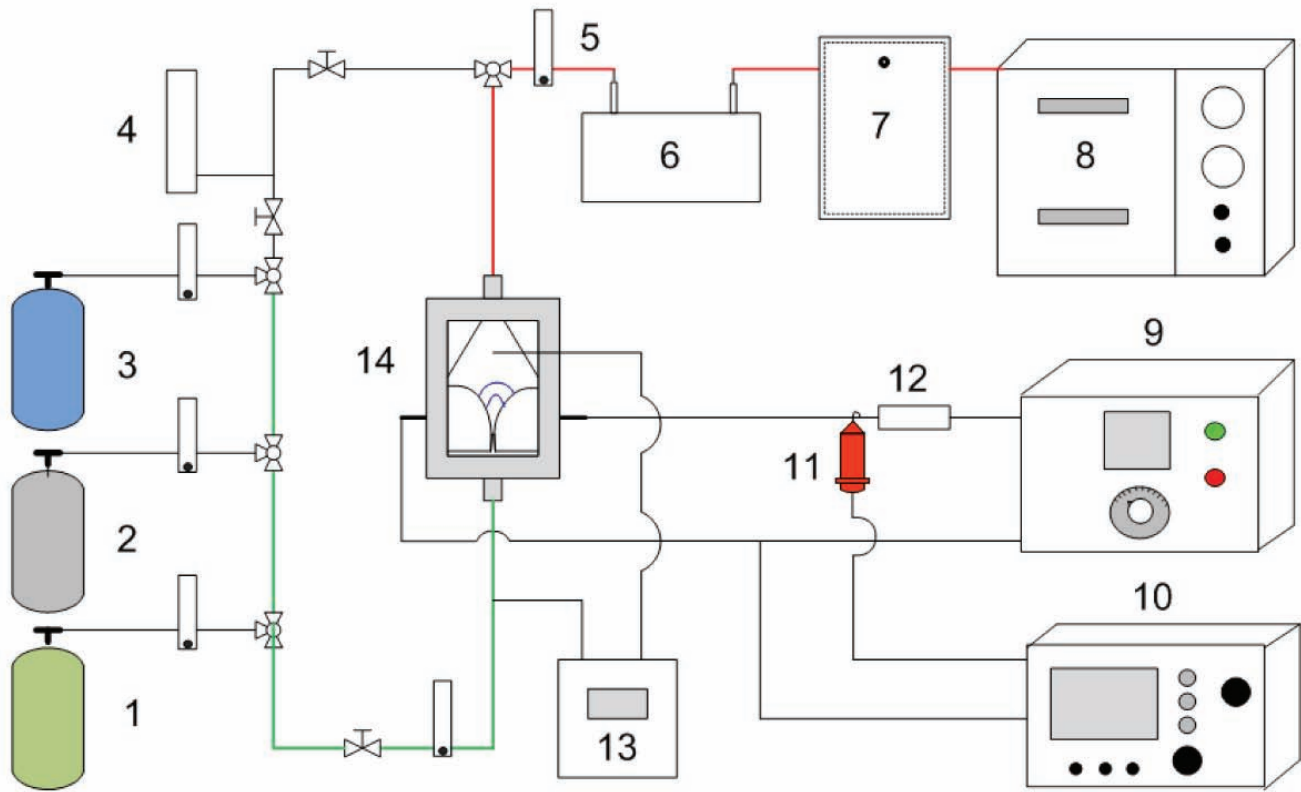


Fig. 1. Schematic diagram of the experimental setup. (1. methane, 2. carbon dioxide, 3. air, 4. bubble flow meter, 5. flow meter, 6. filter and silica gel, 7. gas collection bag, 8. GC, 9. HV power supply, 10. oscilloscope, 11. HV probe, 12. electrical resistance, 13. digital thermometer, 14. gliding arc reactor)

$$\text{H}_2 \text{ yield: } Y_{[\text{H}_2]} (\%) = \frac{M_{[\text{H}_2, \text{produced}]}}{2 \times M_{[\text{CH}_4, \text{in}]}} \times 100 \quad (10)$$

$$\text{CO yield: } Y_{[\text{CO}]} (\%) = \frac{M_{[\text{CO}, \text{produced}]}}{2 \times (M_{[\text{CH}_4, \text{in}]} + M_{[\text{CO}, \text{in}]})} \times 100 \quad (11)$$

Applied energy density:

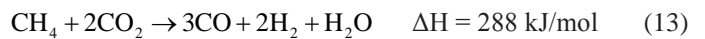
$$\text{AED (kJ/L)} = \frac{\text{AP}}{\text{FR}} \quad (12)$$

where $M_{[\text{CH}_4, \text{in}]}$ is amount of CH_4 input, $M_{[\text{CH}_4, \text{out}]}$ is amount of CH_4 out, $M_{[\text{CO}_2, \text{in}]}$ is amount of CO_2 input, $M_{[\text{CO}_2, \text{out}]}$ is amount of CO_2 out, $M_{[\text{H}_2, \text{produced}]}$ is amount of H_2 produced, $M_{[\text{CH}_4, \text{converted}]}$ is $\text{CH}_{4[\text{in}]} - \text{CH}_{4[\text{out}]}$, $M_{[\text{CO}, \text{produced}]}$ is amount of CO produced, AP is power or input electricity in kW, FR is feed gas flow rate in L/s, respectively.

3 Results and Discussion

Effects of CH_4/CO_2 and CH_4/O_2 molar ratios in plasma assisted partial oxidation on H_2 and CO yields and selectivities, as well as CH_4 and CO_2 conversions were considered. They are shown in Figs. 2 to 4. Biogas composition was varied (CH_4/CO_2 : 50/50, 70/30, 90/10), such that enrichment of methane was taken into account. In this work, large range of CH_4/O_2 molar ratios (0.5 - 20) was considered. For a fixed and very low

value of CH_4/O_2 ratio, enriching CH_4 content or decreasing CO_2 content in biogas was found to produce higher yield and selectivity of H_2 , while no clear pattern was emerged for yields and selectivity of CO, as well as conversion of CH_4 and CO_2 . Maximum H_2 yield of over 25% was obtained at $\text{CH}_4/\text{CO}_2 = 90/10$, whereas at $\text{CH}_4/\text{CO}_2 = 50/50$, around 10% was observed. There were no significant changes in H_2 yields and CH_4 conversions with increasing CH_4 content for the CH_4/O_2 ratios beyond two. It may be noted that greater presence of CO_2 in biogas seemed to encourage higher CO yields and selectivity as well as higher CH_4 conversion. Possible reaction of biogas reforming at high concentration of CO_2 is [20,21];



Increased CO yields were observed with decreasing content of O_2 . However, in this work, the observed changes were relatively small.

Increasing the CH_4/O_2 ratio was found to affect the performance of the plasma reformer significantly. This was contributed to the fact that an increase in CH_4/O_2 ratio resulted in having less O_2 available to react with the fuel molecules, leading to lower conversion of CH_4 , and yields of H_2 and CO. For the biogas with $\text{CH}_4/\text{CO}_2 = 90/10$, changing the CH_4/O_2 ratios from about 1 to 10 led to declines in CH_4 conversion and H_2 yield

from 45 to 15%, and 25 to 10%, respectively. The highest H_2 yield and CH_4 conversion were obtained at the lowest CH_4/O_2 ratio considered. Optimum condition was found at CH_4/CO_2 of 90:10 and CH_4/O_2 of 1.2 for the maximum CH_4 conversion and H_2 yield of 45.7 and 25.3%, respectively.

With respect to the effect on the selectivities of H_2 and CO, it was found that CO selectivity decreased while H_2 selectivity increased with increasing CH_4/O_2 molar ratio. This was in line with Sreethawong et al. [15]'s observation. The plasma system appeared to promote two spontaneous reactions; partial oxidation of CH_4 and the coupling reaction. The former reaction was favorable at very low CH_4/O_2 ratios, while the coupling reaction and the hydrogenation become more pronounced with increasing CH_4/O_2 ratios [15]. At high CH_4/O_2 ratios (> 10), change in oxygen availability did not significantly affect partial oxidation of CH_4 . At the extremely rich fuel-to-air mixture where oxygen is in short supply, the reaction was expected to behave like dry CO_2 reforming of CH_4 [10]. It should be noted that small traces of moisture as well as H_2S are normally found in biogas, especially from animal farms. Their influences on reforming reaction should not be overlooked. These impurities may affect the performance of the process considered. However, this is outside the scope of the present investigation.

Table 1 shows the comparison of the performance for partial oxidation of CH_4 at the optimum conditions between the gliding arc, dielectric barrier, and corona discharge reactors. The gliding arc plasma systems appeared to show similar ranges of CH_4 conversion, H_2 and CO selectivities. Against other types of discharge, the gliding arc consumed much lower applied energy per unit flow rate than the dielectric barrier discharge system [22], but exhibited higher CH_4 conversion. Corona discharge [23] gave highest H_2/CO ratios of 2.5 and 3.4, compared to 1.8 – 2.0 found in this work.

As far as energy consumption is concerned, the energy utilized in this work was calculated to be 6.0 kJ/L or MJ/m³ of feed gas. For a biomethane with CH_4/CO_2 of 90:10, its calorific value is estimated about 38.3 MJ/kg or 28 MJ/m³, assuming biomethane density of 0.73 kg/m³. Hence, the energy utilized was approximately 20% of the energy contained in the feed gas. The current CH_4 conversion was high, around 45%, in comparison with other plasma sources reported in the literature. Nonetheless, to achieve higher conversion of methane in this plasma reactor setup, the following modifications may be needed; (i) using higher applied energy to generate more energetic active species to encourage higher conversion, (ii) combining the plasma reactor with a catalytic reformer, (iii) passing the reactants into many stages of the reactor in cascade, and (iv) increasing the feed gas injector size. The latter two modifications would increase total residence time of the feed gas within the reactor, which will result in higher conversion. So far, reactor development with regards to the gliding arc plasma reactor remains at laboratory level. Scaling up of the plasma reactor is not yet

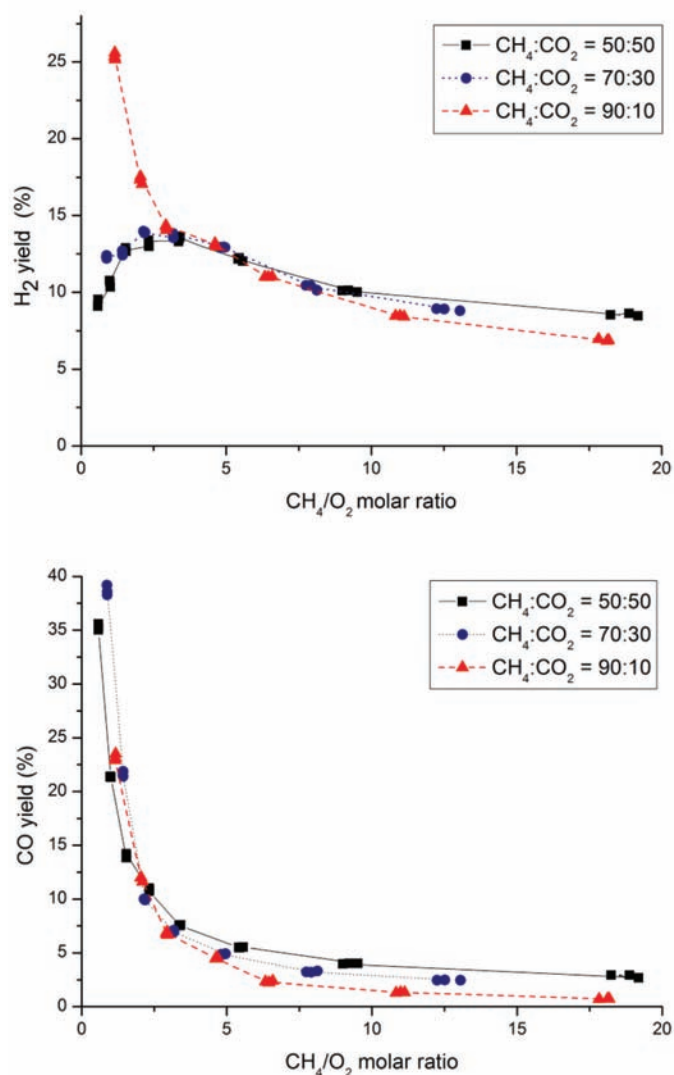


Fig. 2. Effects of CH_4/CO_2 and CH_4/O_2 on H_2 and CO yields.

achieved in realization of industrial plants. Works on the previously mentioned modifications, investigation on other critical factors associated with fluid dynamics and transport properties, as well as process modeling and analysis should be further carried out, prior to development into pilot and industrial units.

4 Conclusions

Gliding arc plasma is a promising technology for biogas reforming into useful products. In this work, a gliding arc discharge system was utilized in partial oxidation of biogas with air to generate synthesis gas. Effects of varying composition and CH_4/O_2 molar ratio on performance of the plasma reformer were investigated. For very low CH_4/O_2 molar ratio, CH_4 conversion and H_2 yield were high. At higher CH_4/O_2 molar ratios, CH_4 conversion and synthesis gas yields decreased. The optimum condition of the gliding arc plasma system was found at CH_4/CO_2 of 90:10 and CH_4/O_2 of 1.2 for the maximum CH_4 conversion. The gliding arc plasma system proved to successfully generate high synthesis gas yields at low energy consumption.

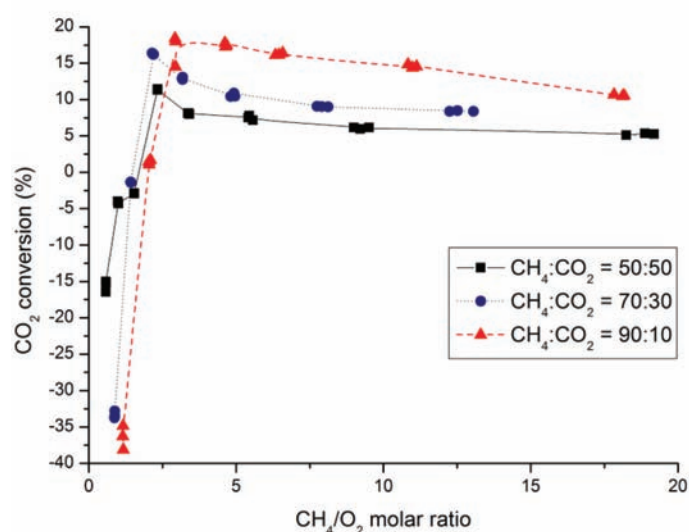
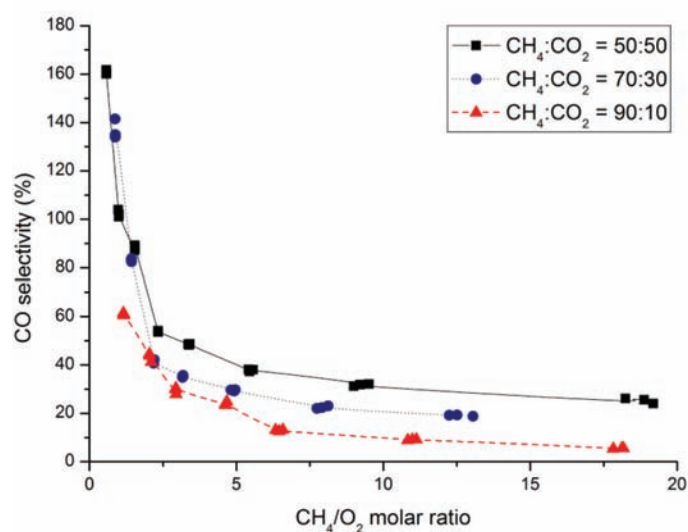
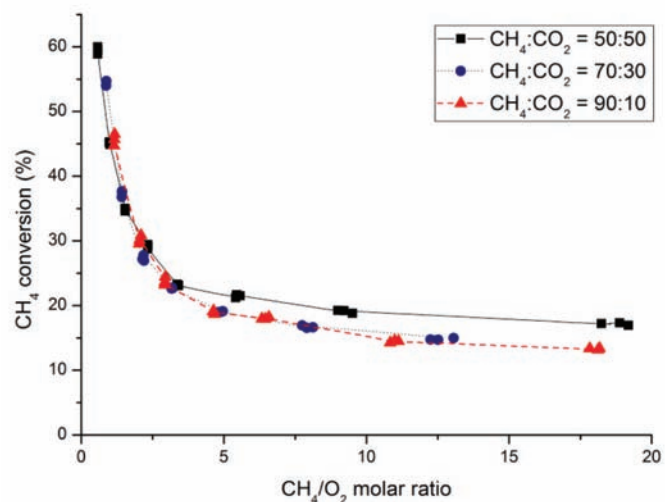
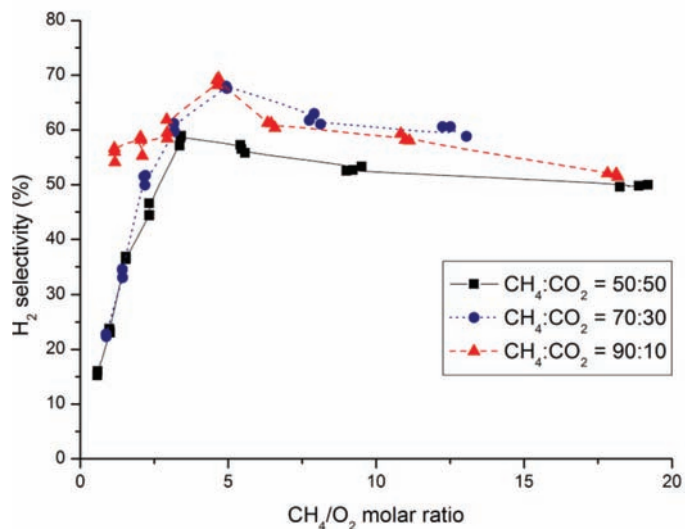


Fig. 3. Effects of CH_4/CO_2 and CH_4/O_2 on H_2 and CO selectivities.

Fig. 4. Effects of CH_4/CO_2 and CH_4/O_2 on CH_4 and CO_2 conversions.

Tab. 1. Comparison with literature on plasma assisted, partial oxidative reforming of methane.

Parameters	This study		[15]		[22]		[23]	
discharge	Gliding arc		Gliding arc		Dielectric barrier		Corona	
feed, CH_4/CO_2	1	2.33	9	3	3	pure CH_4	pure CH_4	pure CH_4
CH_4/O_2	3.4	2.2	1.2	3	3	2	10	3
flow rate (L/min)	1	1	1	0.15	0.15	0.02	0.02	n/a
AED (kJ/L)	6	6	6	n/a	n/a	15	15	n/a
power input (kW)	0.1	0.1	0.1	n/a	n/a	0.005	0.005	0.016
number of reactors	1	1	1	1	4	1	1	1
exit temperature (K)	523	543	573	473	473	n/a	n/a	373
H_2 yield (%)	13.6	13.9	25.3	n/a	n/a	4	5	n/a
CO yield (%)	7.6	10.0	23.1	n/a	n/a	6	6	n/a
H_2/CO	1.8	2.0	2.0	1.3	1.4	n/a	n/a	2.5
H_2 selectivity (%)	58.9	51.2	56.7	46	37	n/a	n/a	62
CO selectivity (%)	48.7	41.6	56.0	32	28	n/a	n/a	n/a
CH_4 conversion (%)	23.1	27.1	45.7	12	45	19	16	38

References

- Aggarangsi P., Tippayawong N., Moran J. C., Rerkkriangkrai P., *Overview of livestock biogas technology development and implementation in Thailand*. Energy for Sustainable Development, 17(4), 371-377 (2013).
DOI: [10.1016/j.esd.2013.03.004](https://doi.org/10.1016/j.esd.2013.03.004)
- Sakar S., Yetilmezsoy K., Kocak E., *Anaerobic digestion technology in poultry and livestock waste treatment: a literature review*. Waste Management & Research, 27(1), 3-18 (2009).
DOI: [10.1177/0734242X07079060](https://doi.org/10.1177/0734242X07079060)
- Nasir I. M., Ghazi T. I. M., Omar R., *Anaerobic digestion technology in livestock manure treatment for biogas production: a review*. Engineering in Life Sciences 12(3), 258-269 (2012).
DOI: [10.1002/elsc.201100150](https://doi.org/10.1002/elsc.201100150)
- Tippayawong N., Thanompongchart P., *Biogas quality upgrade by simultaneous removal of CO₂ and H₂S in a packed column reactor*. Energy, 35(12), 4531-4535 (2010).
DOI: [10.1016/j.energy.2010.04.014](https://doi.org/10.1016/j.energy.2010.04.014)
- Ryckebosch E., Drouillon M., Vervaeeren H., *Techniques for transformation of biogas to biomethane*. Biomass and Bioenergy, 35(5), 1633-1645 (2011).
DOI: [10.1016/j.biombioe.2011.02.033](https://doi.org/10.1016/j.biombioe.2011.02.033)
- Wilhem D. J., Simbeck D. R., Karp A. D., Dickenson R. L., *Syngas production for gas-to-liquids application: technology, issues and outlook*. Fuel Processing Technology, 71(1-3), 139-148 (2001).
DOI: [10.1016/S0378-3820\(01\)00140-0](https://doi.org/10.1016/S0378-3820(01)00140-0)
- Rostrup-Nielsen J. R., *Syngas in perspective*. Catalysis Today, 71(3-4), 243-247 (2002).
DOI: [10.1016/S0920-5861\(01\)00454-0](https://doi.org/10.1016/S0920-5861(01)00454-0)
- Tao X., Bai M., Li X., Long H., Shang S., Yin Y., Dai X., *CH₄-CO₂ reforming by plasma: challenges and opportunities*. Progress in Energy and Combustion Science, 37(2), 113-124 (2011).
DOI: [10.1016/j.peccs.2010.05.001](https://doi.org/10.1016/j.peccs.2010.05.001)
- Vanugopalan M., Veprek S., *Kinetic and Catalysis in Plasma Chemistry*. in 'Recent Synthetic Developments in Polyquinane Chemistry' (L. A. Paquette) Springer-Verlag, New York, Vol. 119. 1-58 (1983).
- Thanompongchart P., Tippayawong N., *Progress in plasma assisted reforming of biogas for fuel gas upgrading*. American Journal of Scientific Research, 76, 70-87 (2012).
- Mutaf-Yardimci O., Saveliev A. V., Fridman A. A., Kennedy L. A., *Thermal and nonthermal regimes of gliding arc discharge in air flow*. Journal of Applied Physics, 87(4), 1632-1641 (2000).
DOI: [10.1063/1.372071](https://doi.org/10.1063/1.372071)
- Petitpas G., Rollier J.-D., Darmon A., Gonzalez-Aguilar J., Metkemeijer R., Fulcheri L., *A comparative study of non-thermal plasma assisted reforming technologies*. International Journal of Hydrogen Energy, 32(14), 2848-2867 (2007).
DOI: [10.1016/j.ijhydene.2007.03.026](https://doi.org/10.1016/j.ijhydene.2007.03.026)
- Fridman A., Nester S., Kennedy L. A., Saveliev A., Mutaf-Yardimci O., *Gliding arc gas discharge*. Progress in Energy and Combustion Science, 25(2), 211-231 (1998).
DOI: [10.1016/S0360-1285\(98\)00021-5](https://doi.org/10.1016/S0360-1285(98)00021-5)
- Chun Y. N., Song H. O., *Syngas Production Using Gliding Arc Plasma*. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 30(13), 1202-1212 (2008).
DOI: [10.1080/15567030600817670](https://doi.org/10.1080/15567030600817670)
- Sreethawong T., Thakonpatthanakun P., Chavadej S., *Partial oxidation of methane with air for synthesis gas production in a multi-stage gliding arc discharge system*. International Journal of Hydrogen Energy, 32(8), 1067-1079 (2007).
DOI: [10.1016/j.ijhydene.2006.07.013](https://doi.org/10.1016/j.ijhydene.2006.07.013)
- Yang Y.-C., Lee B.-J., Chun Y.-N., *Characteristic of methane reforming using gliding arc reactor*. Energy, 34(2), 172-177 (2009).
DOI: [10.1016/j.energy.2008.11.006](https://doi.org/10.1016/j.energy.2008.11.006)
- Rafiq M. H., Hustad J. E., *Experimental and thermodynamic studies of the catalytic partial oxidation of model biogas using a plasma-assisted gliding arc reactor*. Renewable Energy, 36(11), 2878-2887 (2011).
DOI: [10.1016/j.renene.2011.04.012](https://doi.org/10.1016/j.renene.2011.04.012)
- Rafiq M. H., Hustad J. E., *Synthesis gas from methane by using a plasma-assisted gliding arc catalytic partial oxidation reactor*. Industrial & Engineering Chemistry Research, 50(9), 5428-5439 (2011).
DOI: [10.1021/ie102260r](https://doi.org/10.1021/ie102260r)
- Rafiq M. H., Jakobsen H. A., Hustad J. E., *Modeling and simulation of catalytic partial oxidation of methane to synthesis gas by using a plasma-assisted gliding arc reactor*. Fuel Processing Technology, 101, 44-57 (2012).
DOI: [10.1016/j.fuproc.2011.12.044](https://doi.org/10.1016/j.fuproc.2011.12.044)
- Seyed-Matin N., Jalili A. H., Jenab M. H., Zekordi S. M., Afzali A., Rasouli C., Zamaniyan A., *DC-pulsed plasma for dry reforming of methane to synthesis gas*. Plasma Chemistry and Plasma Process, 30(3), 333-347 (2010).
DOI: [10.1007/s11090-010-9225-8](https://doi.org/10.1007/s11090-010-9225-8)
- Chun Y. N., Yang Y. C., Yoshikawa K., *Hydrogen generation from biogas reforming using a gliding arc plasma-catalyst reformer*. Catalysis Today, 148(3-4), 283-289 (2009).
DOI: [10.1016/j.cattod.2009.09.019](https://doi.org/10.1016/j.cattod.2009.09.019)
- Nozaki T., Hattori A., Okazaki K., *Partial oxidation of methane using a microscale non-equilibrium plasma reactor*. Catalysis Today, 98(4), 607-616 (2004).
DOI: [10.1016/j.cattod.2004.09.053](https://doi.org/10.1016/j.cattod.2004.09.053)
- Supat K., Chavadej S., Lobban L. L., Mallinson R. G., *Combined steam reforming and partial oxidation of methane to synthesis gas under electrical discharge*. Industrial & Engineering Chemistry Research, 42(8), 1654-1661 (2003).
DOI: [10.1021/ie020730a](https://doi.org/10.1021/ie020730a)